STATUS OF COAL ASH BEHAVIOR RESEARCH

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INTRODUCTION

The inorganic impurities in coal are converted to ash during combustion and gasification. The problems associated with ash in combustion and gasification systems include deposition on refractory and heat-transfer surfaces, corrosion and erosion of system parts, fine particulate that is difficult to collect, and maintaining slag flow in slagging systems. An overview of ash formation and deposition in utility boilers was performed by Benson and others (1993).

In recent years, significant advances have been made in understanding and predicting the behavior of ash in combustion and gasification systems. These predictions are based on a detailed knowledge of ash formation and deposition mechanisms that have been obtained through bench-, pilot-, and full-scale testing. The mechanisms have been elucidated through the use of advanced methods of coal and coal ash analysis. These techniques are based on scanning electron microscopy and microprobe analysis to determine both the chemical and physical characteristics of coal minerals, fly ash, agglomerates, and deposits. Several methods to predict ash behavior are being developed, including advanced indices and phenomenological models. The analytical methods and predictive methodologies have been described in detail by Benson and others (1993).

This paper summarizes Energy & Environmental Research Center (EERC) work that has been accomplished on ash-related research pertaining to coal-fired utility boiler and provides a brief overview of ash issues related to emerging and advanced technologies that utilize coal. Much of the discussion focuses on the behavior of ash produced from lower-ranked coals, such as lignites and subbituminous from the U.S.

ASH FORMATION

Depending upon the severity of the process, the inorganic impurities can go through significant physical and chemical transformations. Physical transformations involved in high-temperature suspension- or entrainment-type combustion and gasification systems include 1) selective elemental vaporization and subsequent reaction/condensation to form surface coatings or homogeneous fine particulates, 2) coalescence of mineral grains within hot reactive char particles, 3) char fragmentation and partial coalescence of included minerals, 4) shedding of particles from the char surface, 5) fragmentation or fusion of liberated mineral grains, 6) convective transport of volatile species within and between char/mineral particles, and 7) formation of thin-walled ash spheres known as cenospheres. The typical result of these interactions is an ash having a multimodal size distribution, including larger particles that resemble the inorganic constituents in the parent coal and a very fine submicron fractionate resulting from condensation and fragmentation. Some liberated minerals with high melting temperatures, such as quartz (SiO_2), are carried through a reactor in their original angular form. However, at high temperatures, the bulk of the total inorganic content, made up of silicate and aluminosilicate particles, in dynamic association with other condensed or fused phases, will tend to form molten glassy spheres.

The extent to which different elements initially vaporize and subsequently remain in the vapor state depends on their original association in the coal, the process temperature, and the gas composition (e.g., oxidizing or reducing, water vapor concentration, HCl concentration). In general, alkaline earth elements (Ca, Mg) will tend to remain primarily in a condensed form. Silica and alumina can only be volatilized as suboxides in a reducing atmosphere, causing their vapor or submicron fume to play a very minor role in combustion systems, but possibly a significant role in gasification. The fraction of potassium originally present in illite-type clays tends to be retained in the bulk aluminosilicate ash, as evidenced by the high temperatures (up to 1350°C) required to revolatilize potassium from combustion fly ash (Sondreal, Gronhovd, and Severson, 1985). All available evidence indicates that the sodium in low-rank coal (along with the organically associated potassium) is substantially vaporized and subsequently distributed throughout a reactor system, primarily as a surface coating on ash particles or as discrete particles (with enrichment in finer particle-size fractions), but also as a persistent vapor under certain conditions of concern in advanced power systems.

Reactions of organically associated alkali and alkaline earth elements are initiated by the decomposition of carboxylates to form carbonates between 400° and 600°C (Stewart, Stinespring, and Davidovits, 1982). At higher temperatures, the carbonates are believed to decompose to metal oxides that are subsequently reduced to metal vapor by carbon monoxide or char. In a quadrupole mass spectrometry profile of a laboratory-pulverized lignite–air flame, vapor-phase sodium atoms appeared first, followed by vapor-phase sodium hydroxide

(Greene and O'Donnell, 1987). Quenched sampling of an entrained flow combustion reactor operated on Montana lignite indicated that up to 80% of the coal sodium was vaporized and converted to a submicron fume at 1900 K (1627°C, 2961°F) (Neville and Sarofim, 1985). Up to 20% of the magnesium and a small percentage of the calcium were vaporized (Quann and Sarofim, 1986).

Thermal reaction products from discrete mineral grains in low-rank coals produced by laboratory ashing (oxidation in air) at temperatures between 250° and 1300°C include the major x-ray diffraction (XRD) groupings (Falcone and Schobert, 1986; Falcone, Schobert, Rindt, and Braun, 1984). Laboratory thermogravimetric analysis (TGA) and differential thermal analysis (DTA) have also been used to study phase transformations as a function of temperature (O'Gorman and Walker, 1973). With heating in air, clays first lose their absorbed interlayer water between 50° and 150°C. Gypsum ($CaSO_4 \cdot 2H_2O$) dehydrates in this same temperature range, first to bassanite ($CaSO_4 \cdot \frac{1}{2}H_2O$) and then to anhydride ($CaSO_4$) at 180°C. Clay structures are further dehydrated and collapsed by loss of hydroxyl water between about 350° and 600°C, with attending substitution of cations derived from carboxylates, carbonates, oxides, and sulfates into the structure. The oxidation of pyrite (FeS) to produce iron oxides occurs between 325° and 620°C, and calcite ($CaCO_3$) decomposes to calcium oxide between 700° and 830°C. Quartz is stable up to 1000°C. Various glassy and amorphous phases are observed at 1300°C. The amorphous glass and liquid phases have special importance as bonding agents in high-temperature sintered deposits. In crystalline materials the structural units observed for some of the common silicate systems typical of many lower-rank coal deposits are summarized in Table 1.

The crystallization behavior of ashes and slags can provide insight into the temperature at which the deposit or fly ash formed. In addition, crystallization from a liquid phase changes the composition of the residual liquid and that influences its physical properties. This is extremely important in determining slag viscosity. The temperature of critical viscosity, T_{cv}, is the temperature when crystallization from the liquid phase occurs. This crystallization causes the flow characteristics to go from a Newtonian liquid to a non-Newtonian liquid.

Sulfates also contribute to the formation of deposits in combustion systems. The sulfate phases form as a result of the reaction of SO_3 with alkali and alkaline earth elements such as sodium and calcium, respectively. Sulfates are formed primarily by vaporization and condensation processes. During combustion, sulfur oxides form primarily from the oxidation of sulfides and organic sulfur in the flame. At the high temperatures in a flame, sulfur dioxide forms first followed by the formation of sulfur trioxide. At lower temperatures, equilibrium favors the formation of SO_3. Sulfur oxides can interact with the surface of fly ash particles. It has been shown that the maximum amount of reaction occurs between sulfur oxides and ash at approximately 560°C and is dependent upon the quantity of alkali and alkaline earth oxides in the ash. The exact way alkali and alkaline earth sulfates form in combustors appears to be poorly understood. It is assumed that the alkali elements volatilize in the flame and are converted to oxides. The alkali oxide then reacts with SO_2 and O_2 or SO_3 to form sulfates. It has been postulated that sulfates form in the gas stream and condense on the surfaces of materials such as fly ash particles or boiler steel surfaces. Another possible path for the reaction is on the surface of entrained fly ash particles where an alkali layer (NaOH) is first deposited and the subsequent sulfur oxide interaction.

ASH DEPOSITION AND AGGLOMERATION
Pulverized Coal Combustion
Ash deposition mechanisms in pulverized coal combustion systems have been extensively investigated by the EERC under sponsorship of industry consortia (Benson and others, 1988, 1992; Hurley and others, 1992). At the microscopic level observable by scanning electron microscope point count (SEMPC) techniques developed at the EERC, ash deposits in combustion systems are shown to be caused by sodium-rich glass/liquid cementing phases and recrystallized alkaline earth aluminosilicates at temperatures above about 1900°F (1038°C) and by low melting sulfate-rich phases that bond deposits at lower temperatures. Sodium enrichment of the aluminosilicate-based amorphous phase is the foremost cause of the low liquid-phase viscosity and sintering that characterize severe fouling at higher temperatures. This type of ash deposition has been successfully modeled by a viscous flow sintering mechanism, where the growth and strength of the deposit are directly related to the amount of the liquid phase and inversely proportional to its viscosity.

At temperatures below 1900°F (1038°C), the thermodynamic equilibrium shifts to allow sulfation of alkali and alkaline earths, leading to several modes of ash deposition when high-calcium coals are burned in pc-fired boilers. Laboratory strength tests and SEM observations indicate that calcium sulfate crystals form an interlinked lattice that imparts strength over periods of 1 to 10 days, with more rapid strength development occurring at higher temperatures up to 1850°F (1010°C), at higher ratios of total alkali to silica ($(Na_2O + K_2O + MgO + CaO)/SiO_2$), and with more uniform diffusion of SO_2 through the deposit. Deposits formed on leading edge tube banks just below 1900°F rapidly become sulfated and hard. Tubes downstream of this screening action are coated with calcium-rich enamel-like deposits that are hard upon deposition and formed from particles smaller than about 3 μm. Loose powdery deposits formed on the downstream side of tubes, by ash particles smaller than

10 μm being trapped in gas eddies behind the tubes, are somewhat stronger at higher gas velocities and correspondingly smaller, affected particle sizes. A low-temperature engineering algorithm of deposition risk (LEADER) has been developed at the EERC to predict low-temperature deposition.

Fluidized-Bed Combustion

The FBC process consists of two subprocesses: a) the fluidization of solids, by which solid particles/granules are suspended in an upward flowing stream of gas and b) the combustion process, in which fuel particles are burned to sustain temperature. The solids in FBCs are typically fuel ash, bed material, sorbent used to control pollutants, and reaction products formed by sulfur capture and other sorbent–coal interactions. FBC systems operated at atmospheric pressure are classified as atmospheric fluidized-bed combustors (AFBCs), which usually also denotes low fluidization velocities resulting in a bubbling bed. Circulating fluidized-bed combustors (CFBCs) operate at fluidization velocities approximately 7 to 8 times higher. At these velocities, the rising gas entrains the bed materials; the resulting bed consists of a turbulent cloud of solids that fills the combustion chamber. A portion of the bed material is continuously carried out with the offgas and recirculated back to the combustion chamber. Pressurized fluidized-bed combustion (PFBC) systems are similar to AFBCs, but operate under pressure. The compressed air used contains more oxygen per unit volume and, therefore, sustains a higher intensity of combustion, allowing for the design of smaller combustors. The other principal advantage of the PFBC is the increased conversion efficiency (coal-to-electricity) that can be achieved by passing the hot, pressurized combustion gases through both a gas turbine and a waste-heat boiler serving a steam turbine to extract more usable energy in a combined cycle system.

Although FBCs typically operate at low temperatures (1450° to 1700°F), evidence from pilot, industrial, and utility boilers indicates that certain ash components have the potential to cause ash-related problems. These problems can manifest themselves as agglomeration and sintering of the bed material or as deposition on the heat exchanger tube surfaces.

Agglomeration, sintering, and deposition have all been observed in a number of operational FBCs (Steen and Imsdahl, 1989; Makansi, 1988; Miller, 1988; Mann and others, 1992). Analytical results of samples from these various units indicate that the material that forms the initial layers on the bed material, in the case of agglomeration, and on tube surfaces, in the case of deposition, is the result of the presence and behavior of sodium- and potassium-rich calcium sulfates. The sodium, potassium, and sulfur are readily volatilized during combustion and condense on the cooler surfaces. Calcium released from the coal during combustion also reacts with the sulfate matrix. This sulfate matrix may be molten at the operating temperatures of the fluid bed and serve to glue particles together in the form of agglomerates or form thicker deposits. The sulfate matrix sinters over time to form a strongly bonded deposit.

Certain requirements are necessary for these phenomena to occur. The fuel must contain alkali or alkaline earth elements that can be liberated during combustion. Organically bound elements are typically liberated during combustion and have been shown to be the major precursors to in-bed tube deposition and agglomeration. In addition, competing reactions with other coal mineral components can reduce the alkali availability. The fate of these potential deposit- and agglomerate-forming minerals will ultimately influence the extent of deposition and agglomeration. Therefore, it is important to understand the nature of the mineral matter in the original coal so that improvements can be made in the prediction of FBC performance.

Bed material agglomeration is the process which causes relatively small bed particles to stick together, forming larger masses of material. Coal ash reacting with bed material forms the substance which acts as the "glue" in agglomeration. These ash-related interactions occur under normal FBC-operating conditions and include the formation of low melting eutectics between sodium-, potassium-, calcium-, and sulfate-rich components and, possibly, some solid-solid reactions. Agglomeration can also occur as a result of localized hot spots of bed material, where temperatures in the FBC system can exceed the typical 1700°F limit. Temperatures capable of melting various ash species can be attained even during relatively stable operation of the FBC.

A very fine-grained coal ash matrix deposited on in-bed superheat surfaces has been noted in both pilot facilities and utility-scale systems. This deposition is related to the coal ash chemistry and has been observed in stations operating with a bed temperature as low as 1450°F, despite the high erosive forces of bed material in a bubbling fluid bed. The mechanism of adherence and growth appears to be via a molten sulfate matrix, due to the fluxing action of alkali.

Coal Gasification

In coal gasification systems, the coal is converted to a combustible gas, volatiles, char, and ash/slag. Coal gasification has been technically and economically feasible for many years. Commercial gasifiers differ widely in the way in which they produce ash, and either a dry ash, an agglomerated ash, or slag may result. The Lurgi and other fixed-bed gasifiers

operate by passing air or oxygen and steam under pressure up through a bed of coal, which is fed to the top of the bed through a lock hopper. Coal and char move to the bottom as they are gasified, and the dry ash is removed through a bottom grate. Alternatively, a fixed-bed gasifier can be designed to operate at high temperatures, producing a bottom slag that is tapped through a hearth, i.e., the British Gas Lurgi (BGL) process. Fluidized-bed gasifiers, including the U.S. Kellogg Rust Westinghouse (KRW) and Institute of Gas Technology (IGT) processes and the German Winkler process, operate in a gasification mode using steam and air or oxygen in a fashion resembling PFBC. Either dry ash or a fused agglomerated ash may be produced depending on the design, operating temperatures, and the fusion temperature of the ash. Entrained flow gasifiers, including Dow, Texaco, and Shell designs, all operate at very high temperatures and produce a vitreous slag. Integrated gasification combined cycle (IGCC) systems directly link these various types of gasifiers with a gas turbine/steam turbine cycle to achieve high conversion efficiency.

In a dry ash fixed-bed gasifier or grate-type combustor, bed temperatures are maintained below the fusion temperature of the ash, and the bulk of the ash along with a substantial part of the coalesced vapor and liquid species are consolidated in the grate discharge. In very high-temperature slagging gasifiers and combustors, all of the physical transformations described are operative, but the consolidation of ash and slag depends on reactor configuration. In a fixed-bed slagging reactor (e.g., the BGL gasifier), virtually all of the inorganic reaction products are recaptured in the relatively cool descending fuel bed and consolidated into the slag discharge. In an entrained flow reactor (e.g., Texaco, Dow, and Shell gasifiers or cyclone-type combustors), slag is partially separated by impingement or cyclonic action while a (potentially small) fraction is carried forward with the hot gas.

The chemical, mineralogical, and physical characteristics of gasifier ash have been investigated (Eklund, 1986; McCarthy and others, 1985; Stevenson and Larson, 1985; Hassett and others, 1985), and the characteristics of ash produced from the Shell pilot-scale testing (Mahagaokar and others, 1990) and Texaco testing (EPRI, 1990) have been reported. Slag/ash samples have been characterized from eight gasifiers (Eklund, 1986). The types of materials examined included coarse ash or slag and cyclone dust. The materials were found to be nonhazardous, but the physical characteristics and chemical compositions varied significantly as a function of process configuration, operation, coal feed composition, and coal handling. The elemental compositions of the slags produced in gasification systems were similar to the bottom ash from conventional coal combustion systems (Turner and Lowry, 1983). The bulk compositions of cyclone dust samples were found to be similar to conventional coal combustion fly ash (Wetzel and others, 1982). The mineralogical examination of slags (McCarthy and others, 1985) indicated that many of the same high-temperature silicate minerals are present in the slag samples along with reduced iron-bearing compounds. The key difference in coal gasification ash and slag compared to combustion ash is the lack of sulfur. Sulfur is present in small quantities in the ash, usually in the form of a sulfide. In addition, the other ash species in the system may also be in reduced form. The entrained-flow slagging gasifiers recycle all fly ash back to the vitreous slag. Slag samples produced in the Shell process (Mahagaokar and others, 1990) were shown to be depleted in several trace elements. The fine fly slag contained carbon and a higher level of trace metals.

Slagging Combustors and Direct-Fired Gas Turbines
A pressurized slagging combustor coupled with hot-gas cleaning is a potentially simple system for producing hot gas for a gas turbine combined cycle. The major problems encountered in using coal directly as a gas turbine fuel are due to the inorganic components in the fuel. Direct-fired slagging combustors offer potential capital cost savings for coal-fired combined cycle systems, but only if the hot gases generated can either be used directly or economically cleaned to remove particulates, sulfur, and alkalies. A slagging combustor direct-fired gas turbine system is being tested and so is a three-stage slagging combustor (Lecren and others, 1992). The ash by-products produced from these systems are a vitreous slag and the particulate collected in collection devices. Slagging combustors retrofit to a package boiler (Zauderer and Fleming, 1991) were able to produce a vitreous slag with relatively high ash retention. The fly ash produced was chemically and physically similar to typical pulverized coal fly ash. The fine particulates generated from volatilized inorganic components or organically associated inorganics in low-rank coals would be expected to reduce the percentage of total ash that could be removed in the slag cyclone or impactor alone, thereby adding to the need for a barrier filter. High-alkali coals would likely require alkali gettering. In reference to controlling sulfur along with slag, the reported high levels (up to 90%) of nonequilibrium sulfur captured on limestone in the reducing section of a slag combustor have, in fact, provided no more than about 50% sulfur control overall, even with rapid slag removal, owing to reemission of sulfur at high temperature under more fuel-lean conditions (Diehl and others, 1992). Sulfides that may occur in reduced slag would pose problems in either use or disposal, possibly requiring subsequent oxidative treatment. Calcium sulfide produces poisonous and odoriferous hydrogen sulfide on contact with water.

Externally Fired Combined Cycle Systems
Externally fired combined cycle systems, based on currently available gas turbine technology supporting a turbine inlet temperature of 2500°C when using air as the working fluid, offer potential efficiencies of 47% to 50%, fired either on coal alone or on a combination of coal and

natural gas. Accordingly, DOE is vigorously pursuing a system development program, Combustion 2000, based on high-temperature coal-fired air heaters using advanced ceramic materials such as high-density silicon carbides (SiC) and SiC–alumina blends. Lead contractors for Combustion 2000 are United Technologies (Seery, 1993) and Foster Wheeler (FW) (Shenker and McKinsey, 1992), with a separate program being pursued by Hague International (Vandervort and Orozco, 1992). The generic system configuration includes a high-temperature advanced furnace consisting of the combustor, slag screen, radiant and convective air heaters, and a heat recovery steam generator, together with the gas turbine/steam turbine combined cycle power system and conventional SO_x and particulate control modules. The FW system uses a series of three air heaters fired on coal char, pyrolysis gas, and natural gas. Low NO_x emissions in these various systems would be achieved by combustion controls, using staging (rich–lean) or aerodynamically controlled mixing. Combustion 2000 aims at commercial demonstration by 1999 of an ultraclean system for achieving a minimum efficiency of 47% operating on a wide range of coals. The characteristics of the ash and slag from these systems will likely be similar to those found in conventional combustion systems. Higher carbon contents may be found in the ash owing to the low-NO_x combustion technologies under consideration.

SLAG AND ALKALI ATTACK ON CERAMIC MATERIALS

Candidate ceramic materials used in hot particulate filters and heat exchangers are subject to corrosive attack by molten slag and alkali vapor, augmented by other agents including sulfur oxides, sulfides, chlorides, hydrogen, steam, carbon monoxide, char, and ceramics impurities. Failures of ceramic filters in short-term tests conducted to date, up to about 1000 hours, are attributed primarily to mechanical flaws in design or manufacturing; long-term reliability over a desired service life of 10,000 hours will be largely determined by stability to chemical attack. Candidate materials include both oxides, such as mullite, alumina, and cordierite, and non-oxides, such as silicon carbide and silicon nitride, in various bonded matrices. Extensive research is continuing to understand the synergistic interaction of chemical, thermal, and mechanical failure mechanisms (Alvin and others, 1991; Vass and others, 1990). The corrosive mechanisms which have special relevance to low-rank coals are those involving alkali vapors and low-viscosity basic slags.

Alkali attack on aluminosilicates such as mullite occurs by formation of low melting alkali–silica glassy phases on surfaces and in grain boundaries, involving the same types of chemical reactions as occur in ash deposition; resistance to alkali attack is increased by increasing alumina content up to about 60%. Silicon carbide and silicon nitride materials suffer alkali attack when the protective surface layer of silica resulting from passive oxidation during manufacture and later use is converted to an alkali–silica glassy phase, exposing the unprotected SiC and Si_3N_4 surface to further oxidation and alkali attack. In other contributing mechanisms, hydrogen and steam can cause silica volatilization in reduced (SiO) or oxidized (H_2SiO_4) states, and the decomposition of carbon monoxide to carbon at 400° to 700°C can lead to the chemical reduction of iron oxide impurities in ceramics, triggering iron-based catalytic disintegration reactions. These various mechanisms are strongly temperature-dependent, but all are significant at or above the 1600°F (871°C) maximum operating temperature of first-generation ceramic filters and at the 2000°–2500°F (about 1100°–1400°C) temperatures of structural or insulating refractories used in direct coal-fired turbine combustors and heat exchangers for externally fired combined cycle systems. The phase changes resulting from chemical attack together with thermal cycling lead to volume expansion, cracking, spalling, viscous creep, loss of mechanical strength, and eventual structural disintegration. Susceptibility to progressive corrosive attack can be critically influenced by the viscosity of the melts and coal–ash slags on refractory surfaces. Chemically basic slags from some low-rank coals exhibit a rapid reduction in viscosity over a relatively narrow range of temperature increase. Tests at Oak Ridge National Laboratory on heat exchanger ceramics at temperatures up to 2260°F (1238°C) (Ferber and Tennery, 1981) indicated that the most corrosion-resistant (silicon carbide) material survived 500 hours of exposure without degradation under a dry acidic slag, but was severely attacked by a runny basic slag. However, differences in the reported corrosion resistance of various ceramics suggest that subtle differences in the slag composition may play an important role that is unexplained by the currently available data or theory.

SUMMARY AND CONCLUSIONS

The advances made over the past several years in understanding ash behavior in coal utilization systems have been made possible as a result of more detailed and better analysis of coal and ash materials. These advanced techniques are able to quantitatively determine the chemical and physical characteristics of the inorganic components in coal and ash (fly ash and deposits) on a microscopic scale. Many of the mechanisms of ash formation, ash deposition, and ash collection in pulverized coal combustion systems are more clearly understood as a result of these new data. This understanding is leading to the development of better methods of predicting ash behavior in pulverized coal combustion systems. Currently, these same methods are being applied to emerging and advanced coal utilization technologies.

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TABLE 1
Crystalline Forms and Examples of Specific Crystal Species (Benson and others, 1993).

Crystalline Forms	Structural Units	Examples
Orthosilicates	$(SiO_4)^{-4}$	Fayalite - Fe_2SiO_4
Pyrosilicate	$(Si_2O_7)^{-6}$	Melilite (Gehlenite-Alkermanite) $Ca_2Al_2SiO_7 \cdot Ca_2MgSi_2O_7$
Metasilicate	$(SiO_3)_n$	Pyroxenes (Diopside - Augite) $CaMgSi_2O_6 \cdot Ca(Fe, Mg)Si_2O_6$
Framework Silicates	Al^{3+} replaces Si^{4+} in tetrahedra	Plagioclase (Albite - Anorthite) $NaAlSi_3O_8 \cdot CaAl_2Si_2O_8$